



Products distribution during the gas phase photocatalytic oxidation of ammonia over the various titania based photocatalysts

P.A. Kolinko*, D.V. Kozlov

Borisevsk Institute of Catalysis, pr. Ac. Lavrenteva 5, Novosibirsk 630090, Russia

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ABSTRACT

The adsorption and photooxidation of gaseous ammonia have been investigated by the FTIR spectroscopy method in a static reactor using TiO₂ and modified TiO₂ as photocatalysts. Two types of modified TiO₂ were tested: TiO₂ impregnated with transition metal oxides (NiO, V₂O₅, MoO₃, and Fe₂O₃) and TiO₂ doped with noble metals like Ag, Au, Pt, Pd by the chemical and photochemical deposition methods. Molecular nitrogen, NO₃[−], N₂O and water were found as the major final products of ammonia photocatalytic oxidation (PCO). One of the purposes of the current study was to minimize the N₂O formation during PCO. The pure unmodified TiO₂ (anatase, S_{BET} ~ 350 m²/g) turned out to be the best photocatalyst for this purpose giving only 7% of initial NH₃ quantity converted into N₂O. Long-term experiments were carried out to determine the photocatalysts stability in PCO of NH₃. All the catalysts exhibited stable performance; the rate of deactivation was low due to the transformation of NH₃ nitrogen mainly into N₂. Only ~30% of initial NH₃ quantity was oxidized into HNO₃ which was adsorbed on the catalysts surface in all cases.

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1. Introduction

Ammonia is the major air pollutant in the production of nitrogen fertilizers, agriculture, stock-breeding and especially poultry farming. Agricultural workers are exposed to huge ammonia concentrations resulting in numerous on-the-job respiratory diseases [1]. In addition, NH₃ is evolving from the urea containing antifreeze admixtures used for the depression of concrete freezing point in the building construction. So it is today an actual problem of air purifying from ammonia. A well-known TiO₂ mediated photocatalytic oxidation (PCO) method was chosen for this purpose for its universality and ability to mineralize almost any acescent substance [2,3]. Titanium dioxide is well known as a photocatalyst for the elimination of environmental pollutants and is a harmless white powder [4,5]. The TiO₂ photocatalyst absorbs photons with wavelengths below 400 nm and promotes redox reactions on its surface. The photocatalytic activity of TiO₂ was applied for NO_x removal [6], water splitting [7], decomposition of VOC [8], etc., on a laboratory scale.

Italian scientists [9] demonstrated significant decrease of gaseous NH₃ concentration in a farrowing room as a result of TiO₂ mediated photocatalytic oxidation. TiO₂ was sprinkled on the

inside walls of the farrowing room and the irradiation was conducted by the 12 36 W UVA lamps. Dong et al. [10] tested the TiO₂ (Degussa P-25) supported on the woven fabrics for the removal of indoor ammonia.

According to the previous studies [11,12] nitrous oxide (N₂O) should form as one of the final products during NH₃ PCO. The N₂O formation occurs as a result of hyponitrous acid decomposition which in turn forms in the following sequences of reactions:



Nitrous oxide could form not only during the ammonia PCO but also other N-containing species like unsymmetrical dimethylhydrazine (H₂N–N(CH₃)₂) which was reported in our previous work [13].

N₂O is an important greenhouse gas with a lifetime of about 150 years in the atmosphere. It has about 310 times higher greenhouse potential than CO₂ [14], and contributes to the destruction of the ozone layer in the stratosphere [15]. N₂O destruction occurs in the stratosphere by photolysis and oxidation and it is also an important source of stratospheric nitrogen oxides (NO_x) which initiate a chain of cyclic reactions leading to ozone destruction [16,17]. In this way the limitation of N₂O emissions has become a

* Corresponding author. Tel.: +7 383 3331617; fax: +7 383 3331617.

E-mail address: kolinko@catalysis.ru (P.A. Kolinko).

significant target in the control of anthropogenic emissions. So the first purpose of present study was to find the most suitable photocatalysts which minimize the N_2O output during NH_3 PCO. Another subject for investigation was the photocatalysts stability during numerous cycles of NH_3 PCO.

2. Experimental

2.1. Materials

The ammonia (gas 99.8%), $(\text{NH}_4)_2\text{MoO}_4$ (high-purity grade, REACHIM), $\text{Fe}_2(\text{SO}_4)_3$ (high-purity grade, REACHIM), NH_4VO_3 (high-purity grade, REACHIM), $\text{Ni}(\text{NO}_3)_2$ (high-purity grade, REACHIM), AgNO_3 (high-purity grade, REACHIM), H_2SO_4 (high-purity grade, REACHIM), EtOH (high-purity grade, Hippocrat), H_2PtCl_6 and HAuCl_4 (REACHIM) were used as supplied without further purification. Distilled water purified with Bärnsted “Easy pure II” ultra pure water system ($\Omega = 18.2 \text{ M}\Omega/\text{cm}$) was used in all syntheses.

TiO_2 (Sachtleben Chemie, 100% anatase, $S_{\text{BET}} = 347 \text{ m}^2/\text{g}$, average pore diameter 4.9 nm) was used as pure photocatalyst and as further starting agent for the synthetically modified photocatalyst.

2.2. Modification of the TiO_2 surface

Different TiO_2 based photocatalysts were synthesized in the present work by TiO_2 impregnation with transition metal oxides (NiO , V_2O_5 , MoO_3 , and Fe_2O_3) and TiO_2 doping with noble metals like Ag, Au, Pt, Pd by the chemical and photochemical deposition methods.

TiO_2 impregnation by metal oxides was conducted according to the following method. A 5 g of TiO_2 was placed in a 150 ml round-bottom flask and a 100 ml of aqueous solution with necessary metal salt ($\text{Fe}_2(\text{SO}_4)_3$, $(\text{NH}_4)_2\text{MoO}_4$, NH_4VO_3 , $\text{Ni}(\text{NO}_3)_2$) was added. Concentrations of $\text{Fe}_2(\text{SO}_4)_3$, $(\text{NH}_4)_2\text{MoO}_4$, NH_4VO_3 , $\text{Ni}(\text{NO}_3)_2$ were equal to 3.12×10^{-3} , 3.47×10^{-3} , 5.5×10^{-3} , $6.67 \times 10^{-3} \text{ M}$ correspondingly so that after the mild water evaporation at 40°C in the Petri dish and subsequent powder annealing at 770 K for 3 h the metal oxides content should be equal to 1, 0.1 and 0.01 wt.% for each of $\text{Fe}_2\text{O}_3/\text{TiO}_2$, $\text{MoO}_3/\text{TiO}_2$, $\text{V}_2\text{O}_5/\text{TiO}_2$ and NiO/TiO_2 catalysts.

Ag, Au and Pt metals deposition were conducted by the TiO_2 impregnation with AgNO_3 , HAuCl_4 or H_2PtCl_6 corresponding water solutions with subsequent reduction (chemical or photo-assisted). This procedure was described in detail previously [18]. There were synthesized Ag/ TiO_2 and Au/ TiO_2 photocatalysts containing 1 wt.% of Ag or Au by the photo-assisted reduction method and Ag/ TiO_2 , Au/ TiO_2 and Pt/ TiO_2 photocatalysts containing 1 wt.% of Ag or Au and 0.5 wt.% of Pt by the chemical reduction method.

2.3. FTIR in situ experiments

All TiO_2 samples for FTIR in situ experiments were prepared as follows. The TiO_2 water suspension treated with ultrasound during 15 min time interval was uniformly deposited onto the CaF_2 glass (diameter 20 mm and thickness 1 mm) and dried at room temperature. The TiO_2 powder density in obtained samples was $\approx 1 \text{ mg}/\text{cm}^2$.

These samples were placed in the thermostatic reactor mounted in the cell compartment of FTIR spectrometer (Thermo, NICOLET 380) which was described previously [19]. The main feature of the reactor is the possibility of measuring either IR spectra of the gas phase or the TiO_2 catalyst surface with adsorbed species during the PCO process. All IR spectra were measured in the $900\text{--}4000 \text{ cm}^{-1}$ region with the 2 cm^{-1} resolution and the accumulation of 16 scans. All experiments were carried out in atmosphere of air cleared from CO_2 and water. Therefore in all

experiments oxygen with a percentage of 23 mass% was contained. An airflow of $100 \text{ cm}^3/\text{min}$ of $\approx 0\%$ relative humidity was passed through the reactor with the installed sample for 1 h. Then, 1 ml of gaseous NH_3 at 1 bar pressure was usually injected into the reactor before PCO. Relative humidity $\approx 0\%$ was used for this purpose that all experiments passed in identical conditions.

The high pressure Hg lamp DRSH-1000 (Russia) was used as UV light source. Sample irradiation was conducted by condensed light passed through water filter (major line $\lambda \sim 365 \text{ nm}$, $W = 20.8 \text{ mW}/\text{cm}^2$). The measurement of light intensity was conducted by the microvolt meter F-136 (Russia) equipped with the semiconductor light intensity detector calibrated with the ferrioxalate actinometer [20].

2.4. Surface species analysis

The detection of final products and intermediates of the NH_3 PCO adsorbed on the photocatalyst surface was conducted by the analysis of water rinsed from the photocatalyst. The ion chromatography method with Metrohm 861 (Advanced Compact IC) instrument was used for rinsing water analysis and detecting inorganic ions. Eluent was $3.2 \text{ mM Na}_2\text{CO}_3$, 1.0 mM NaHCO_3 , volume of selected test $20 \mu\text{L}$, flow rate $0.7 \text{ ml}/\text{min}$ in column A supp 5 ($250/4.0 \text{ mm}$).

The rinsing of surface species was done according to the following method. A 3 mg of deposited photocatalyst was gently transferred from the CaF_2 glass support into the 20 ml glass beaker and then the 10 ml of deionized water was added. Then the suspension was sonicated for the 5 min time interval and left for 1 h for surface species desorption. To be assured of full removal ions from the surface, the measurement of adsorption these ions on the catalyst surface in similar conditions has been made. The metering curve has been constructed using results of adsorption.

3. Results and discussion

3.1. FTIR study of NH_3 PCO with the pure unmodified TiO_2

After the injection of 1 ml gaseous NH_3 (pressure 1 bar) into the IR cell and subsequent setting of the adsorption equilibrium between gas phase and photocatalyst surface the sample irradiation was started and the IR spectra of gas phase and photocatalyst surface were registered periodically for PCO results monitoring. As measurement of concentration, we used “ppm” as one million part of atmospheric pressure.

Fig. 1 demonstrates the changes of gas phase IR spectra during NH_3 PCO on the pure unmodified TiO_2 . The 3336 cm^{-1} absorption band corresponds to the valence symmetrical vibration $\nu_s(\text{N-H})$ in the NH_3 molecule whereas 2224 cm^{-1} absorption band corresponds to the valence symmetrical vibration (ν_s) in the N_2O molecule [21]. The formation of water could be seen from the rotational component of the same gaseous IR spectra in the $3550\text{--}3900 \text{ cm}^{-1}$ range where the increase of $\nu(\text{O-H})$ absorption bands intensities corresponds to the gaseous water formation. So the formation of gaseous N_2O and H_2O and ammonia disappearance during the NH_3 PCO with the pure unmodified TiO_2 was observed in the gas phase.

Using the integral form of Lambert's absorption law¹ it is possible to calculate the concentrations of gaseous NH_3 and N_2O from the IR spectra (Fig. 1) [22]. A_0 values for ammonia and nitrous oxide were determined in separate experiment and turned out to be $A_{0(3320\text{--}3341 \text{ cm}^{-1})} = 2.664 \times 10^{-6} \text{ ppm}^{-1} \text{ cm}^{-2}$ and $A_{0(2150\text{--}2260 \text{ cm}^{-1})} = 4.722 \times 10^{-4} \text{ ppm}^{-1} \text{ cm}^{-2}$ for NH_3 and N_2O , respectively. The obtained data from IR spectra gave us the

¹ $A = A_0CL$, where A : the area of an absorption band (cm^{-1}), L : optical pathlength (cm), C : gas concentration (ppm) and A_0 : aspect ratio ($\text{ppm}^{-1} \text{ cm}^{-2}$).

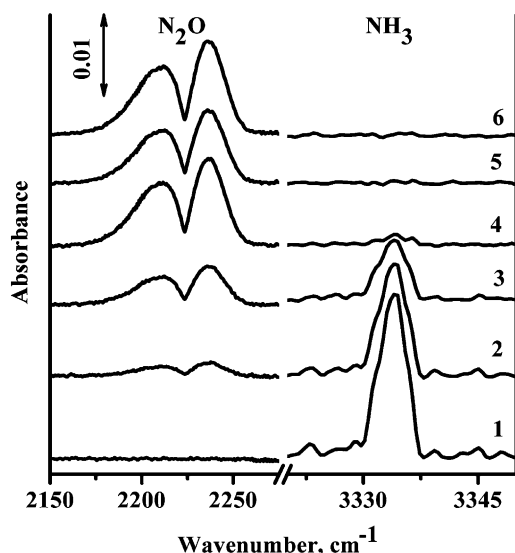


Fig. 1. FTIR spectra of the gas phase during the 1 ml NH_3 portion PCO in the IR cell ($T = 293$ K, relative humidity $\approx 0\%$, reactor volume 300 ml). Figures above spectra correspond to the following times of measurement: 1, before irradiation was started; 2, 15 min; 3, 30 min; 4, 60 min; 5, 90 min; 6, 120 min.

typical kinetic of N_2O accumulation and NH_3 disappearance during the TiO_2 mediated ammonia PCO (Fig. 2). The initial NH_3 pressure is $P_0 \approx 2600$ ppm before irradiation was started whereas calculated initial pressure P_{calc} should be equal to 3330 ppm in the absence of adsorption. It means that about 730 ppm or 22% of injected ammonia was adsorbed on the TiO_2 surface in the beginning.

The complete removal of ammonia occurs for the first 60 min of PCO resulting in the formation of $P_{\text{fin}} = 120$ ppm of gaseous N_2O . If one will calculate the conversion of ammonia into N_2O one should take into account that each N_2O molecule consists of two nitrogen atoms so the conversion ratio (α) will be in our case $\alpha(\text{N}_2\text{O}) = (2P_{\text{fin}}(\text{N}_2\text{O})/P_{\text{calc}}(\text{NH}_3)) \times 100\% = (2 \times 120/3330) \times 100\% = 7.2\%$.

The formation of adsorbed nitrates was also observed according to IR spectra of the TiO_2 surface during the NH_3 PCO (Fig. 3). It was demonstrated in the previous work [13] that the absorbance in TiO_2 surface IR spectra in the $1280\text{--}1500\text{ cm}^{-1}$ range with the maximums at the 1350 cm^{-1} (bidentate [23]) and 1440 cm^{-1} (monodentate [24]) corresponds namely to HNO_3 adsorbed on the TiO_2 . It is only possible to obtain the qualitative information about

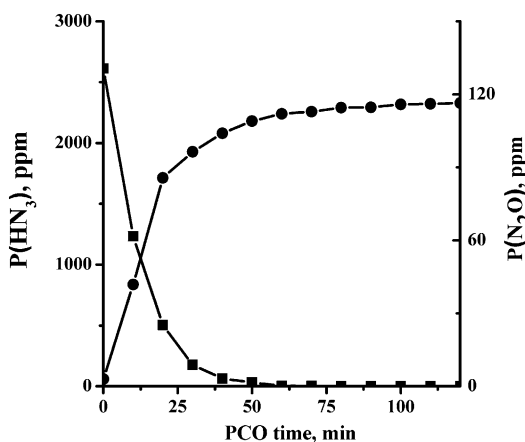


Fig. 2. Kinetic curves of NH_3 (■) vapor removal and N_2O (●) accumulation during the 1 ml gaseous NH_3 PCO. Experimental conditions are the same as indicated in the caption for Fig. 1.

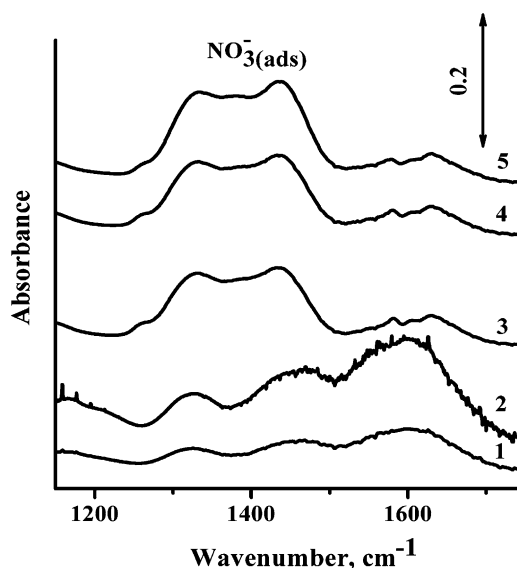


Fig. 3. FTIR spectra of the unmodified TiO_2 surface during the PCO of 1 ml gaseous NH_3 in the 300 ml static reactor. $T = 293$ K, relative humidity $\sim 0\%$. Figures above spectra correspond to the following times of measurement: 1, before irradiation was started; 2, 30 min; 3, 60 min; 4, 90 min; 5, 120 min.

the HNO_3 quantity on the photocatalyst surface during NH_3 PCO and its dynamics. A new band at 1624 cm^{-1} appeared under photoirradiation and grew with time of irradiation. It is well known that this band is assigned to the deformation vibration of H_2O or OH groups interacting with monodentate or bidentate nitrate [25]. In spectra 1 and 2 (Fig. 3) corresponding to the beginning of PCO wide absorption bands near 1600 and 1460 cm^{-1} are corresponding to the deformation vibrations in the NH_3 and NH_4^+ species. The last one forming on the TiO_2 surface as a result of NH_3 interactions with surface Bronsted acid sites.

A series of identical PCO experiments with equal NH_3 portions and photocatalyst samples was conducted to measure the quantitative kinetics of adsorbed species on the photocatalyst surface. Each PCO run was stopped at different times and the surface species analysis with liquid ion chromatograph was conducted. Only nitrates and nitrites were found and kinetics of their quantities change is shown in Fig. 4.

Surface nitrites (NO_2^-) being an intermediate reached its maximum quantity 60 min after the beginning of PCO reaction and completely disappeared after 65 min. Surface nitrate is the product of complete NH_3 mineralization and its quantity constantly risen during PCO and reached its final value $\nu_{\text{fin}}(\text{NO}_3^-) = 9.3 \times 10^{-6}\text{ mol}$ 200 min after the beginning of PCO reaction (Fig. 4).

Equal volumes (1 ml at 20°C) of gaseous NH_3 were used in all experiments; it means that initial NH_3 quantity was equal to $\nu_0(\text{NH}_3) = ((10^{-3}\text{ l}) \times 1\text{ (atm)}) / (0.082\text{ (l atm/mol K)} \times 293\text{ (K)}) = 4.2 \times 10^{-5}\text{ mol}$ in all cases. In this way the ammonia conversion ratio into nitrates is equal to $\alpha(\text{NO}_3^-) = (\nu_{\text{fin}}(\text{NO}_3^-) / \nu_0(\text{NH}_3)) \times 100\% = (9.3 \times 10^{-6} / 4.2 \times 10^{-5}) \times 100\% = 22\%$.

The combination of TiO_2 surface IR spectra with the results of surface species analysis by means of ion chromatography allows further to use only IR spectroscopy for the approximate determination of the adsorbed nitrate quantity as a less laborious technique. In fact the area of the $\text{NO}_3^-(\text{ads})$ absorption band in the $1228\text{--}1520\text{ cm}^{-1}$ range is equal to $S_{1228\text{--}1520}(\text{NO}_3^-(\text{ads})) = 43.8\text{ cm}^{-1}$ (Fig. 3, spectrum 5) and corresponds to the complete ammonia mineralization with the formation of $9.3 \times 10^{-6}\text{ mol}$ of adsorbed nitrates according to ion chromatographic analysis (Fig. 4). On the basis of Lambert's absorption law one can suppose that the quantity of formed adsorbed nitrates $\nu(\text{NO}_3^-(\text{ads}))$ could be expressed through the intensity of the corresponding absorption

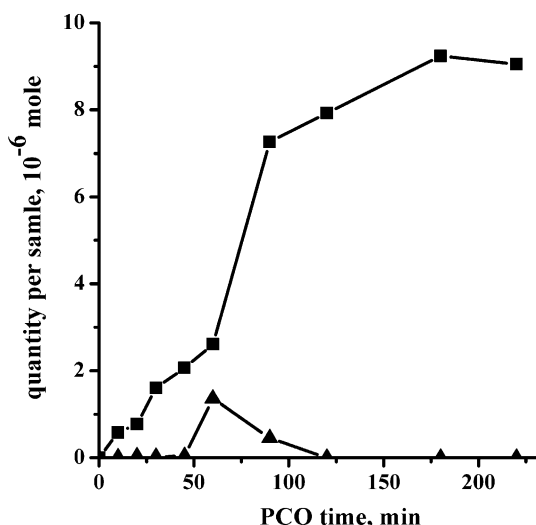


Fig. 4. Kinetic curves of adsorbed nitrates NO_3^- (■) and nitrites NO_2^- (▲) quantities change during the 1 ml gaseous NH_3 PCO on the pure unmodified TiO_2 . Experimental conditions are the same as indicated in the caption for Fig. 1.

band via formula:

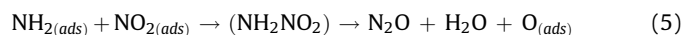
$$\nu(\text{NO}_{3(\text{ads})}^-) (\text{mol}) = \frac{9.3 \times 10^{-6} \text{ mol}}{43.8 \text{ cm}^{-1}} \times S_{1228-1520}(\text{NO}_{3(\text{ads})}^-) \\ = 2.1 \times 10^{-7} \times S_{1228-1520}(\text{NO}_{3(\text{ads})}^-) (\text{cm}^{-1}) \quad (4)$$

Of course formula (4) could be applied only for photocatalyst based on the TiO_2 with minor modifications (<1%) prepared by the same method described in the experimental part.

Since no other nitrogen containing species were detected in the gas phase and on the TiO_2 surface then the last product of NH_3 PCO should be dinitrogen (N_2) and NH_3 conversion ratio into N_2 is equal to $\alpha(\text{N}_2) = 100\% - \alpha(\text{N}_2\text{O}) - \alpha(\text{NO}_3^-) = 70.8\%$. Lee et al. [26] managed to achieve 80% conversion ratio of NH_3 into N_2 but in water phase PCO using Pt modified TiO_2 .

Let us compare kinetics of gaseous and surface species (Figs. 2 and 4). On the one hand the ammonia was completely removed from the gas phase after 60 min of PCO reaction and N_2O pressure reached almost stable level. On the other hand the quantity of the surface NO_3^- species reached only about 40% of its maximum and still was increasing. It means that there was still source of nitrogen somewhere in the reaction system which was transformed into adsorbed nitrates and probably into dinitrogen (N_2) because the last product was not controlled during the PCO reaction.

It is known that particle NH_2 reacts with NO_2^- (nitrites) on the surfaces of the catalyst with the formation of particle NH_2NO_2 that is oxidized to N_2O [27]:

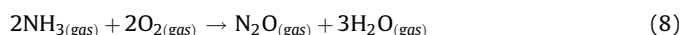
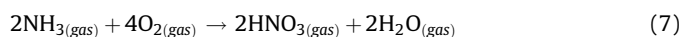
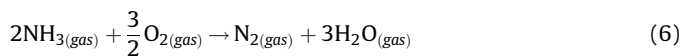


According to the Ramis et al. [28] the adsorption band wave number which could be assigned to the NO-stretching vibration in NH_2NO surface species is equal to 1468 cm^{-1} but in our case (Fig. 3) there is a wide adsorption band corresponding to the adsorbed nitrous acid. This wide band could mask the 1468 cm^{-1} adsorption band.

Therefore, after the removal of ammonia from the gas phase the increase in N_2O stops. At the same time the oxidation of intermediate products to nitrites and finally to nitrates occurs. Therefore, while studying washouts from the surface of the catalyst, we did not observe any nitrites during the initial moment but when the ammonia completely disappears from a gas phase

the formation of surface nitrites begin. Finally the nitrites are oxidized to nitrates which are the only surface products of complete NH_3 PCO.

Based upon the above discussion it could be concluded that ammonia PCO reaction can proceed in three parallel routes giving N_2 , N_2O and HNO_3 as major nitrogen containing products:



Gibbs free energy for these three reactions $\Delta_r G_{298}^0$ was calculated on the basis of data presented in Ref. [30] and turned out to be -652.41 , -585.4 and -548.31 kJ/mol for reactions (6), (7) and (8) correspondingly. The real $\Delta_r G_{298}^0$ value for reactions (6)–(8) should be somewhat lower because some components of reactions and especially nitric acid could adsorb on the catalyst surface but nevertheless as one can see all three products could be formed since there is no thermodynamic prohibition. Moreover, the more profitable reaction is from the thermodynamic point of view the higher is the conversion ratio of ammonia into the corresponding product. Indeed the N_2 is the major product ($\alpha(\text{N}_2) = 70.8\%$) and $\Delta_r G_{298}^0$ for it is equal to -652.41 kJ/mol and vice versa N_2O is the minor product and $\Delta_r G_{298}^0$ for it is equal to -548.31 kJ/mol is the lowest one.

3.2. Ammonia PCO with TiO_2 modified by noble metals and transition metal oxides

Studies of gaseous ammonia PCO using several modified TiO_2 photocatalysts were done analogously with the investigation of ammonia PCO on the unmodified TiO_2 reported in the previous section.

Generally two types of TiO_2 based photocatalysts were studied namely (1) TiO_2 modified with noble metals (Ag, Au, Pd, and Pt) deposited by chemical or photochemical reduction method; and (2) TiO_2 modified with transition metal oxides (Fe_2O_3 , CoO, NiO, V_2O_5 and MoO_3). The purpose of both types of TiO_2 modifications was to improve the TiO_2 adsorption properties against gaseous NH_3 and therefore to raise the rate of ammonia PCO. Modification of TiO_2 with sulfuric acid purposed the same object. Another aim was to reduce the nitrous oxide output.

Sano et al. [31] used Ag/ TiO_2 photocatalyst for the N_2O photocatalytic decomposition but in the presence of methanol vapor. Some other researchers like Satsuma et al. [32] and Henderson et al. [33] investigated the catalytic activity of some transition metal oxides in the nitrous oxide decomposition reaction. As in work [32] they also used reducing agent but methane instead of methanol. Oxygen turned out to inhibit N_2O decomposition reaction due to the lack of oxygen vacancies in metal oxide phase which is necessary for the removal of oxygen from N_2O molecule and the formation of molecular nitrogen. Such oxygen vacancies were found to influence the N_2O decomposition in high vacuum and cannot be formed in ambient conditions because air always contains up to 20% of O_2 . Also the several hundred degree temperatures were needed to achieve the acceptable decomposition rate.

Nevertheless we tried to use TiO_2 based photocatalysts in ambient conditions without the addition of reducing agent to understand the possibility of minimizing the N_2O output during the NH_3 PCO. All results are summarized in Table 1.

The highest activity and ammonia conversion into N_2 and the lowest nitrous oxide output were demonstrated by unmodified high surface area TiO_2 (anatase). Therefore it is the best

Table 1

Catalytic activity of different TiO₂ samples during the 1 ml gaseous ammonia (calculated initial NH₃ pressure $P_{\text{calc}} = 3330$ ppm) PCO in 300 ml static reactor (relative humidity $\approx 0\%$, $T = 293$ K, $W_{\lambda \approx 356 \text{ nm}} = 20.8 \text{ mW/cm}^2$).

Catalyst	Preparation method	Initial NH ₃ pressure, P_0 (ppm)	NH ₃ PCO rate for 30 min starting time interval (ppm(NH ₃)/min)	Part of oxidized NH ₃ for 240 min time interval (%)	Ammonia conversion ratio (α) for 240 min time interval (%) into:		
					N ₂ O	NO ₃ [−] _(ads) based on the surface IR spectra	N ₂
TiO ₂	Unmodified	2610	80.4	100	7	22	71
1% Ag(hv)/TiO ₂	Photoreduction	2510	27.6	100	14	11	75
1% Ag(NaBH ₄)/TiO ₂	Chemical reduction with NaBH ₄	2630	23.3	100	16	11	73
1% Au(hv)/TiO ₂	Photoreduction	3030	26.8	100	27	11	62
1% Au(NaBH ₄)/TiO ₂	Chemical reduction with NaBH ₄	2610	31.8	100	28	24	48
1% Pd/TiO ₂		2360	49.8	100	11	33	56
0.2% Pt/TiO ₂		2800	35.9	100	10	31	58
4M H ₂ SO ₄ /TiO ₂	Pretreated with 4M H ₂ SO ₄ water solution	2840	68.5	100	8	27	65
1% NiO/TiO ₂	Impregnation with water	3040	2.9	35.55	2	1	97
0.1% Fe ₂ O ₃ /TiO ₂	solution of the corresponding	3290	31.8	100	10	86	4
0.5% CoO/TiO ₂	metal salt with following	3150	4.8	37.01	2	24	74
0.01% Fe ₂ O ₃ /TiO ₂	calcinations	3280	39.8	100	10	20	70
0.01% MoO ₃ /TiO ₂		3200	20.8	100	9	53	38
0.01% V ₂ O ₅ /TiO ₂		3120	18.9	100	9	36	55

photocatalyst for being used in commercial air purifiers for ammonia decomposition.

Photocatalysts modified with noble metals with the following chemical or photochemical reduction demonstrated average activity, i.e. the ammonia could be mineralized completely for 4 h time period but the rate of mineralization is lower than for pure TiO₂ and the N₂O production is also higher. The third column in Table 1 shows initial ammonia pressures after the adsorption equilibrium was established in the system. We anticipated the increase of photocatalyst adsorption properties against NH₃ after the metal deposition but it was not observed because the quantity of adsorbed NH₃ ($P_{\text{calc}} - P_0$) was approximately the same as in the pure TiO₂ case. Possible explanation of this fact is that the stability constants of noble metals complexes with ammonia are not high unlike the case with cyanide anions as ligand. That is why in our previous work we successfully used Au and Ag for TiO₂ modification and obtained new very active photocatalysts for HCN PCO [18] but in this work the same approach failed.

All the photocatalysts which contained a lot of additional metal oxide phase (1% NiO/TiO₂, 0.1% Fe₂O₃/TiO₂ and 0.5% CoO/TiO₂) demonstrated very low photocatalytic activity and initial NH₃ PCO rate (<5 ppm/min). At the same time the ammonia adsorption on these samples is also very low because the initial pressure is close to theoretically calculated; it means that the metal oxide phases (NiO, Fe₂O₃ or CoO) block the surface and prevent the ammonia interaction with the photocatalyst active sites.

Photocatalytic activity of photocatalysts containing 0.01% of additional metal phase (Fe₂O₃/TiO₂, MoO₃/TiO₂ and V₂O₅/TiO₂) becomes higher but still about 2–3 times lower than for pure unmodified TiO₂. Probably the same blocking of the TiO₂ surface occurs like in the previous case but to a lesser degree.

Practically for all active photocatalysts about 20–30% of initial ammonia is converted into nitrates and 10–30% into nitrous oxide. Overall conclusion could be made that the closer photocatalyst formula is to the pure high surface area anatase form TiO₂ the more active it would be in the PCO reaction of ammonia.

3.3. Study of TiO₂ stability

Finally we tested the stability of the best revealed photocatalyst which turned out to be purely unmodified TiO₂ in multiple long

time ammonia PCO experiments. It was demonstrated that a photocatalyst deactivation occurs during several PCO runs (Fig. 5).

The deactivation of photocatalyst may develop due to the decrease of the number of active surface sites available for the reaction in several consecutive batch runs over the photocatalyst.

One can see that the NH₃ conversion level remained unchanged and is equal to 100%, although the conversion time necessary to reach this level increased from 50 to 100 min for five PCO runs. The surface nitric acid accumulating during PCO that could be easily detected by the rising of absorption bands in the surface FTIR spectra at 1350 and 1440 cm^{−1} positions is responsible for such deactivation.

In this way 5 ml or 2.1×10^{-4} mol of NH₃ was photocatalytically oxidized by 3 mg or 3.75×10^{-5} mol of TiO₂. It means that each Ti atom worked at least 5.6 times and could work some more. We suppose that the washing of photocatalyst could restore its photoactivity because adsorbed nitric acid was completely removed from the TiO₂ surface during our nitrates measurements in water washed from used TiO₂.

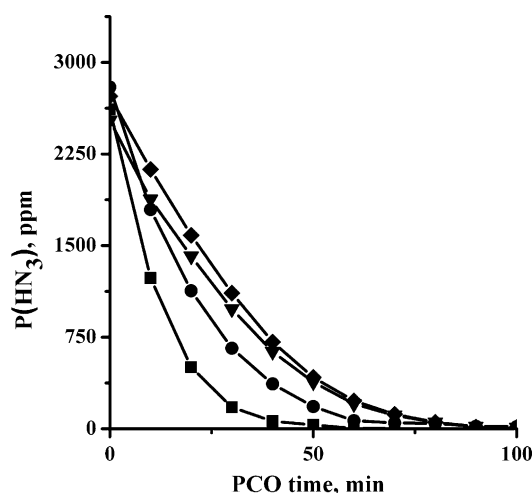


Fig. 5. Kinetic curves of gaseous NH₃ removal during several consecutive PCO runs of equal 1 ml NH₃ portions in the 300 ml static reactor using pure unmodified TiO₂. Symbols ■, ●, ▼, ◆ are corresponding to the first, second, fourth and fifth oxidation runs.

4. Conclusions

The ammonia PCO was investigated for a set of photocatalysts modified with noble metals and transition metal oxides.

Nitrous oxide N_2O was registered as the gaseous PCO product. The formation of dinitrogen N_2 another gaseous PCO product was estimated from the mass balance. Adsorbed nitrites NO_2^- and nitrates NO_3^- were registered as surface intermediates and final products of NH_3 PCO.

The best activity was demonstrated by unmodified high surface area anatase from TiO_2 . This photocatalyst also demonstrated the lowest N_2O production during PCO which is also very important positive feature from the practical point of view. Ammonia was converted into N_2O (7%), N_2 (71%) and adsorbed HNO_3 (22%) by this photocatalyst.

The accumulation of surface nitrates is the possible reason of TiO_2 deactivation during the several consecutive runs of NH_3 PCO. Nevertheless every Ti atom worked at least 5.6 times till the PCO rate decreased in two times.

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